Self-Assembly Ultrathin Films Based on Diazoresins

Jinyu Chen, Lan Huang, Liming Ying, Guobin Luo, Xinsheng Zhao, and
Weixiao Cao*

College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

A monolayer ultrathin film of nitro-containing diazoresin (NDR) was fabricated on mica via a self-assembly technique. The adsorption of NDR on mica at different deposition times was monitored by determining the absorbance of the NDR. It was confirmed that the deposition is rapid and reaches saturation within 2 min. The multilayer ultrathin films composed of NDR as polycation and poly(sodium-*p*-styrene sulfonate) (PSS) as polyanion were fabricated via layer-by-layer deposition. The surface morphology of the multilayer films was observed by atomic force microscopy (AFM). The results show that an ultrathin multilayer film can be obtained by the self-assembly technique. The multilayer films composed of NDR and PSS are photosensitive; under irradiation by UV light, the linkage nature between the layers converts from ionic to covalent, and, as a result, the stability of the film to polar solvents increases.
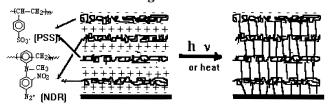
Introduction

Since Iler's pioneering work, a self-assembly technique has been developed to fabricate the layer-by-layer−organized ultrathin films.[1] Via Coulombic attraction, oppositely charged polymers are driven to form an ultrathin film with a two-dimensional structure.[2−4] Because this technique is very simple, easy to automate, and easy to adapt to large-scale application, as well as friendly to the environment,[5] it has attracted more and more attention. Recently, this technique has been developed further and applied to the preparation of advanced membranes, with desired components such as biomolecules,[6] chromophoric molecules,[7] dendritic molecules,[8−10] polymer dyes,[11] conductive polymers,[12] and so forth.

However, because of the Coulombic interaction, the joint force between layers is not strong enough to prevent etching from polar solvents, which will limit the use of this kind of film. This problem can be solved by using a polymerization method or by causing the layers to cross-link.[5,13] Recently, we found that the polyelectrolyte complexes formed from diazoresin as the cationic polyelectrolyte possess a unique characteristic under the influence of UV light, that is, on irradiation by UV light, the complex converts its linkage from an ionic bond to a covalent bond.[14,15] When diazoresins were used as poly-

Scheme 1. Multilayer Film Based on Diazoresin Undergoes Crosslinking under the Influence of UV-Light or Heat

cations, a multilayer thin film was fabricated by a self-assembly technique.[16] The multilayer film fabricated via layer-by-layer deposition, using diazoresins as the cationic polyelectrolyte and various anionic polyelectrolytes, undergoes cross-linking easily upon application of light or heat, as shown in Scheme 1.

In this article, we report the fabrication of thin films using a nitro-containing diazoresin (NDR) formed from 2-nitro-*N*-methyldiphenylamine-4-diazonium salt (NMDS) with formaldehyde as polycation and poly(sodium *p*-styrenesulfonate) (PSS) as polyanion, via a self-assembly technique; properties of these films, especially the stability to polar solvents and surface morphology, are also reported.

Experimental Section

Materials. NDR was prepared in our laboratory according to the method described elsewhere[17] ($\eta_{sp}/c = 0.15$ dl·g^{-1}, Mn ≈ 2500 g/mol). PSS was purchased from ACROS (MW: 100 000 g/mol). Dimethyl formamide (DMF), ZnCl$_2$, and NaCl are analytical agents and were used as received. Sodium dodecyl sulfate (SDS) was recrystallized from ethanol. The water was distilled or deionized. The vessels used were boiled in 50% sulfuric acid, washed with distilled water, and dried.

Preparation of Films. The self-assembly thin films were prepared in the dark at room temperature. The freshly cleaved mica, which has a negative surface, was used as substrate. The mica was first immersed in the NDR aqueous solution (2 mg/mL) for 5 min, washed with deionized water, and dried; it was then dipped into the aqueous solution of PSS (2 mg/mL) for 5 min, followed by rinsing with water and drying in air. This cycle was

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repeated to form the self-assembly multilayer films. To study the relation between time and adsorption mass on the monolayer films, a series of micas were dipped into the NDR solution for a given time (15 s to 40 min), then washed and dried.

Determination of the UV–Vis Spectrum. The absorbance of NDR on mica after every cyclic deposition or after etching in polar solvents was determined using a UV–vis spectrophotometer (Shimadzu 2100). To obtain a flat baseline and reproducible spectra, the micas were cleaved as uniformly as possible. Every measurement was repeated twice. The scan range selected was from 235 to 550 nm.

Solvent Etching. Solvent etching was carried out according to the literature method.[13,18–20] To compare the stability of the film to solvents or solutions containing polar components, both before and after UV-irradiation or heating, the films with 12 bilayers were dipped into aqueous solutions of DMF, NaCl (1 mol/L), or SDS (5 wt%) for different periods of time.

Determination of Surface Morphology. Atom force microscopy (AFM) was used to visualize the surface morphology of the films. The mica on which the ultrathin film was fabricated was adhered to a glass slide for measurement. AFM measurements were performed in air at ambient temperature with the Nanoscopy IIIA (Digital Instruments, Inc.) in the tapping mode. Commercial silicon probes (model TESP-100) with a typical resonant frequency around 300 kHz were used to obtain the image.

Results and Discussion

The NDR Monolayer. The absorbance of a series of NDR monolayers deposited on mica at different deposition times was determined as shown in Figure 1. From Figure 1, we can see that the adsorption of NDR on mica is rather fast and reaches saturation within 2 min. Comparing the surface morphology of the monolayers formed at different deposition times (Figure 2), we see that the polycation was adsorbed on mica in the initial time (<30 s) and was fairly well-distributed. The film exhibits a very even surface. With prolonged deposition time, the thickness as well as the roughness of the films increases (Table 1). This results is somewhat puzzling because the absorbance of the films does not change (see Figure 1).

The adsorption of polymers on substrates has been discussed in many papers.[21–32] Usually, three models—the kinetic control model,[28] the diffusion control model,[30] and the nonequilibrium adsorption model[25]—are used to describe the adsorption process. The former two models are based on equilibrium adsorption, whereas the latter is based on nonequilibrium adsorption and assumes that once a polymer molecule has been adsorbed, it is not at equilibrium.[25] Recently, Tsukruk et al.[31,32] pointed out that in the initial deposition time, nonequilibrium ad-
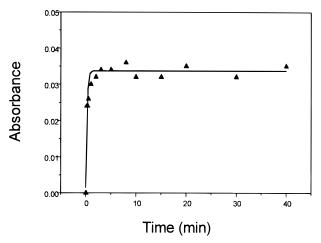
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Figure 1. Absorbance of the NDR monolayer at 383 nm at different deposition times.

Table 1. Average Thickness and Mean Roughness of NDR Monolayers at Different Deposited Times

deposited time (min)	0	0.5	1	5	20
thickness of NDR layer (nm)[a]	0	1.3	1.5	2.0	3.8
mean roughness (nm)[b]	0.32	0.75	0.95	1.4	2.5

[a] Obtained from occasional holes by AFM. [b] Obtained from average high peak to low valley by AFM.

sorption plays an important role due to the strong attraction between polyions and charged substrate and confirmed that only at long deposition times (10–60 min) can an ultrathin film with uniform morphology be obtained. However, the adsorption of NDR on mica forms an even film at initial deposition times (<5 min) rather than at long times (>20 min), as shown in Figure 2. It is difficult to understand that the film's thickness increases and its surface becomes rougher (Figure 2E) with prolonged immersing time, whereas the absorbance does not change. The changes may be caused by the adsorption of counter-ions such as HSO_4^- on the DNR monolayer, but because there is no direct evidence, we think that more experiments should be perfomed.

To calculate the surface coverage of NDR on mica, eq 1 is introduced:

$$\Gamma = A/\epsilon_{surface} \tag{1}$$

where, Γ, A, and $\epsilon_{surface}$ represent the surface coverage, absorbance, and surface extinction coefficient of NDR, respectively. $\epsilon_{surface}$ can be obtained by converting NDR's standard extinction coefficient ($\epsilon_{standard}$) as follows:

$$\epsilon_{surface} \ (mol^{-1} \cdot cm^2) = 1000 \times \epsilon_{standard} \ (M^{-1} \cdot cm^{-1})$$

where the standard extinction coefficient ($\epsilon_{standard}$) of NDR is 2.7×10^4 $(M \cdot cm)^{-1}$, and $\epsilon_{surface}$ is calculated to be 2.7×10^7 $(mol/cm^2)^{-1}$. The saturated absorbance is 0.035 (Figure 1), therefore, the saturated NDR mass deposited on mica (Γ_{sat}) was calculated to be $3.4 \times 10^{-7} g/cm^2$, and the average thickness d of the NDR layer on mica can be calculated approximately to be 2.1 nm from eq 2:

$$d = \Gamma_{sat}/2\rho \tag{2}$$

where ρ is the density of NDR (0.8 g/cm^3), and coefficient 2 was introduced because the deposition takes place on two surfaces of the mica. The calculated value agrees well with that obtained from the AFM determination (2.0 nm from sample deposited 5 min).
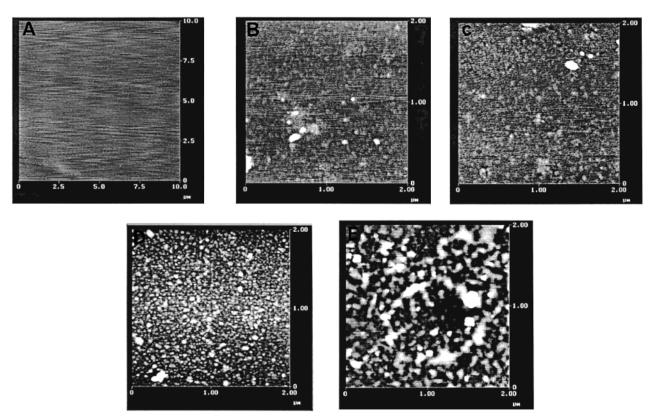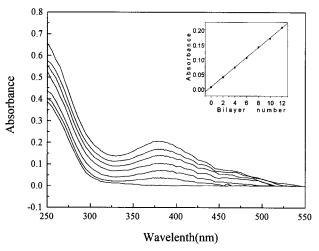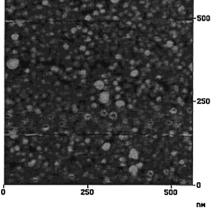
Figure 2. Morphologies of NDR monolayer at different deposited times. Deposition time (minutes): A, 0; B, 0.5; C, 1; D, 5; E, 20.
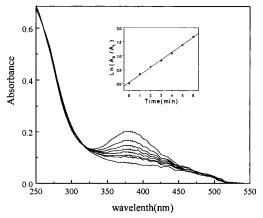

Figure 3. Absorbance of the multilayer film at 383 nm with different numbers of bilayers. Bilayer numbers (bottom to top): 0, 2, 4, 6, 8, 10, 12. Inset plot shows the relationship of absorbance to bilayer number.
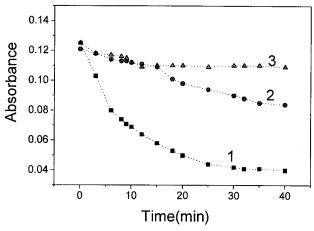
NDR–PSS Multilayer Films. Multilayer ultrathin films from NDR and PSS were prepared, and the absorbance of the films was determined according to the procedure described in the Experimental Section. Figure 3 shows the absorbance increase with increasing bilayer (NDR–PSS layer) numbers. From Figure 3, we can see that the increasing absorbance at 383 nm is about 0.035 for every bilayer and is proportional to the bilayer number; therefore, the adsorption is uniform for every deposition. Figure 4 shows the surface of the first bilayer. The thickness was determined to be 3.5 nm, with a mean roughness of 1.2 nm, by AFM. The NDR layer is 2.1 nm, so the PSS layer should be about 1.4 nm if the NDR layer and PSS layer have no intersection. From the AFM determination, the four-bilayer film (Figure 7A) is rather flat, and the roughness is only 1 nm. Therefore, a flat and

Figure 4. Morphology of the first bilayer of film fabricated by deposition of first NDR, then PSS, each for 5 min. Thickness (nm): 3.5; mean roughness (nm): 1.2.
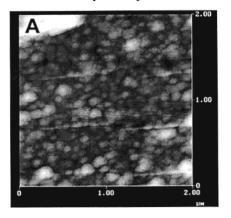

Figure 5. UV–vis spectra of a multilayer film irradiated for different times. Multilayer film: 12 bilayers from NDR and PSS on mica; irradiation intensity: 230 μW cm^2; irradiation time (minute, top to bottom): 0, 1, 2, 3, 4, 5, 6, 30.
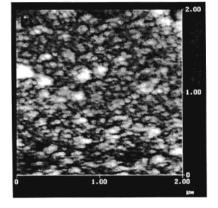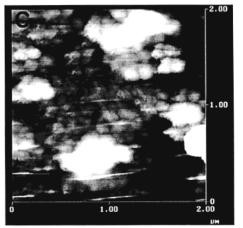
Figure 6. Relationship of absorbance at 383 nm and etching time for the unirradiated multilayer film in different mediums: (1) DMF; (2) NaCl aqueous solution (1 M); (3) SDS aqueous solution (5 wt%). Multilayer film: 12 bilayers from NDR and PSS; etching tempereature (°C): 20.

uniform multilayer film from NDR and PSS can be obtained by the self-assembly technique.

Photoreaction of the Multilayer Film from NDR−PSS. The film with twelve bilayers was fabricated, and the photodecomposition of the film was investigated. The absorbance of the twelve-bilayer film at different irradiation times was determined, as shown in Figure 5. From the $\ln(A_0/A_t)$ versus t plot (inset plot in Figure 5), photodecomposition of the film follows the kinetics of a first-order reaction, where A_0 and A_t (corrected by baseline) represent the absorbance of the film before irradiation and after irradiation for time t, respectively.

Scheme 2. Conversion of Linkage from Ionic Bond to Covalent Bond in the Multilayer Film Formed from NDR and PSS

Under irradiation of UV light, the diazonium groups that link with the sulfonate group via electrostatic attraction decompose to form a phenyl cation, then combine with $-SO_3^-$ to produce a covalent linkage, as shown in Scheme 2. In the self-assembly ultrathin films, $-N_2^+$ and $-SO_3^-$ are bound together via electrostatic attraction. The covalent sulfonate forms following the decomposition of the $-N_2^+$ group, as was verified by IR spectroscopy.[16]

The Stability of Multilayer Films. The effect of irradiation of UV light on the stability of the film to polar solvents or solutions was investigated. Irradiated and unirradiated films were immersed at the same temperature in the solvents or solutions. After a given time, they were drawn out, washed, and dried; the absorbance of the films was then measured at 383 nm. Figure 6 shows the

Figure 7. Etching situation of irradiated and unirradiated multilayer film in the DMF multilayer film, 4 bilayers of NDR−PSS (etching temperature 20 °C): (A) original film (before irradiation and etching); (B) irradiated film (230 μW/cm²; 30 min) and etching in DMF for 30 min; (C) unirradiated film with etching in DMF for 30 min.

absorbance of unexposed twelve-bilayer film at different etching times. From Figure 6, we see that DMF, 1 M NaCl, or a 5% sodium dodecyl sulfate (SDS) aqueous solution can etch the film considerably. For 40 min of etching, the degree of etching (wt%) was determined to be 69%, 27%, and 4%, respectively. However, the exposed film exhibits little etching even after immersion for 24 h in DMF.

The morphologies of the four-bilayer film after and before etching of DMF are shown in Figure 7. The unirradiated film exhibits considerably larger holes and becomes rougher (up to 9 nm mean roughness) after etching for 30 min in DMF, whereas the irradiated film exhibits only a slight change, with a mean roughness of about 3 nm (Figure 7B). The results from both the absorbance determination and the surface morphology indicate that the exposed films have a higher stability to solvent etching. This higher stability is ascribed to the linkage conversion of the NDR−PSS layers from ionic bond to covalent bond.

Conclusion

Using a self-assembly technique, a stable and well-defined monolayer film of NDR and a multilayer film made from NDR and PSS were fabricated. In the monolayer film of NDR, the deposition is very rapid at first and reaches saturation within 2 min. The surface morphology of self-assembly monolayer films at different times exhibits considerable differences, especially at longer deposition times. The absorbance of NDR in the multilayer films increases proportionally with the number of bilayers. Indicating self-assembly really occurs through step-by-step deposition. The surface roughness of the multilayer film decreases with increasing bilayer numbers. A flat and well-organized multilayer film can be obtained with this technique.

Upon UV-irradiation and following the decomposition of the diazonium group, a covalent bond forms between the layers, the multilayer films become more stable and more resistant to etching from organic solvents or solutions.